

Surface passivation-induced enhancement of light absorption in photoanodes for quantum dot-based solar cells

Ho Minh Trung, Le Xuan Thuy

Vinh Long University of Technology Education, Vinh Long, Vietnam

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ABSTRACT

Quantum dot-sensitized solar cells hold promise for low-cost, high-efficiency photovoltaic applications; however, instability due to quantum dot degradation and poor interfacial charge transport remain key challenges. In this study, a copper-doped Zn(S,Se) passivation layer was chemically synthesized and applied onto TiO₂/CdS/CdSe@Cu photoanodes. The goal was to shield quantum dots from corrosive polysulfide electrolytes and enhance photon absorption. The morphology, structure, and optical characteristics of the Zn(S,Se):Cu layers were systematically analyzed using field-emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), and UV–Vis spectroscopy. J–V measurements demonstrated that the ZnSe:Cu-coated photoelectrode achieved a higher power conversion efficiency (5.31%) than the ZnS:Cu counterpart (4.5%). Moreover, electrochemical impedance spectroscopy revealed a lower charge transfer resistance ($R_{ct2} = 331 \, \Omega$), indicating improved electron transport and reduced recombination. These findings highlight the potential of Zn(S,Se):Cu layers in enhancing the stability and efficiency of quantum dot-sensitized solar cells, paving the way for more durable and efficient solar energy devices.

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Corresponding Author:

Le Xuan Thuy

Vinh Long University of Technology Education

Vinh Long, Vietnam

Email: thuylx@vlute.edu.vn

1. INTRODUCTION

Concern about the environment and the need for energy are on the rise. More and more people are interested in studying potential clean energy alternatives to damaging fossil fuels right now. Traditional practices have made extensive use of solar energy for ages, since it is a renewable resource that is generated directly by the sun. Many nations are investing heavily in renewable energy research in an effort to curb carbon dioxide emissions and combat the urgent problem of climate change. There is an immediate need to address the global need for clean, sustainable energy by creating efficient and affordable solar energy systems that can partially replace fossil fuels [1]. Although both dye-sensitized solar cells (DSSCs) and quantum dot-sensitized solar cells (QDSSCs) have layered structures, the benefits of QDSSCs outweigh those of DSSCs. These advantages include, but are not limited to, high absorption coefficients, durability against moisture and oxygen, unique quantum dots with a tunable bandgap energy that can be easily adjusted by controlling particle size [2], and the ability to generate multiple excitons upon photon absorption [3]. Furthermore, QDSSCs are capable of potential conversion efficiencies (PCEs) of up to 44% thanks to these quantum effects [4]. The theoretical PCE of QDSSCs is far higher than the PCE that is currently attained. Nonetheless, QDSSCs' actual PCE remains substantially lower than their theoretical PCE. The poor PCEs of QDSSCs can be attributed to various factors [5]. Surface passivation is another practical method for

improving QDSSCs performance. Passivation of surfaces: By facilitating the separation of electrons and holes, well-designed passivation can restrict dark current and effectively decrease electron recombination. the gloomy stream [6]. Several semiconductor materials, including SiO_2 [6], ZnS [7], and ZnSe [8], are being utilized as surface passivation layers. One of these compounds, zinc selenide (ZnSe), is superior to the others when it comes to creating surface protective layers. By combining ZnS and ZnSe into a surface passivation layer, the Liu lab was able to achieve a 22% gain in efficiency over ZnS alone [9]. Alternatively, Rao's group found that CdS/CdSe quantum dots had an ideal efficiency of 4.18% when Mn was doped into ZnS material to form a surface passivation layer [10]. ZnSe has been extensively utilized for the passivation process of QDSSCs and is one of the inorganic passivation materials that are suited for forming a type II core-shell structure for CdSe/CdS quantum dots owing to its acceptable band structure. It is not possible to absorb light in the long-wavelength regions using ZnSe due to its band gap and desired electrical structure. Doping a material with a transition metal ion, like Mn^{2+} ..., is an effective way to change its energy band structure [11]-[13].

In this study, we fabricated a photonic crystal film based on copper-doped surface passivation layers due to the efficient charge transfer capability of the ions. The structure of the film was analyzed using EDX mapping and XRD; optical properties were evaluated through UV-VIS spectra; the efficiency of QDSSCs was determined through J-V characteristics; morphology and elemental composition were investigated using FESEM. Additionally, the optoelectronic properties are also studied and discussed in detail.

2. METHOD

2.1. Fabrication process of FTO/ TiO_2

The FTO conductive glass was cut into $1.2 \text{ cm} \times 2.0 \text{ cm}$ pieces and cleaned by ultrasonic treatment in distilled water, 0.1 M HCl , and ethanol. The TiO_2 layer was created using the screen-printing method: TiO_2 paste (Dyesol, 20 nm, Anatase) was spread through a mesh onto the conductive glass. Each layer was dried at 120°C for 10 minutes, repeated twice. The film was then gradually heated to 500°C , maintained for 30 minutes, and naturally cooled to obtain a porous TiO_2 film.

Fabrication process of FTO/ TiO_2 /QDs: The FTO/ TiO_2 photoanode undergoes 3 SILAR cycles by alternating dips in 0.1 M Cd^{2+} and 0.1 M S^{2-} for 5 minutes each, rinsed with ethanol and methanol after each dip, then dried at 120°C for 15 minutes. The fabrication of the photoanode and counter electrode is presented in Figures 1 and 2. FTO glass is cleaned, then covered with heat-resistant tape to expose a circular area. It is immersed in a deoxygenated $\text{Cu}^{2+}/\text{S}^{2-}$ solution at 90°C for 30 minutes, rinsed, then annealed at 200°C for 30 minutes and cooled to room temperature. The polysulfide electrolyte ($\text{S}_2/\text{S}_n^{2-}$) is prepared by dissolving Na_2S , S , and KCl (0.5 M, 0.2 M, 0.2 M) in 10 ml distilled water:methanol (7:3), yielding a yellow solution.

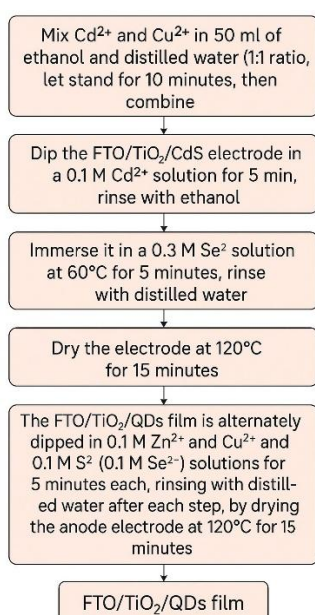


Figure 1. Fabrication diagram of the photoanode electrode

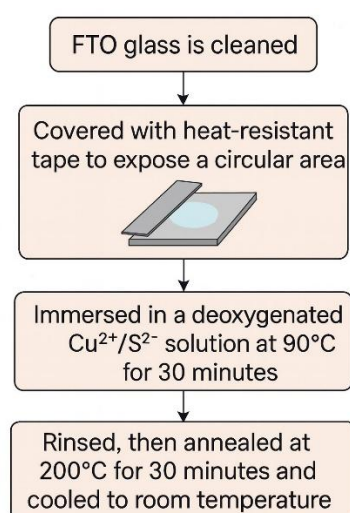


Figure 2. Fabrication diagram of the counter electrode

3. RESULTS AND DISCUSSION

FESEM images (Figure 3) show that the Cu^{2+} -doped X(S,Se) layer deposited on the TiO_2/QDs surface exhibits a uniform distribution of nanoparticles and a porous structure. The incorporation of Cu^{2+} ions reduces the spacing between particles and partially fills the surface pores, resulting in a denser surface morphology. No significant differences are observed between the two samples, except for these changes induced by the presence of Cu^{2+} .

Figure 4 displays the UV-Vis absorption spectrum of the FTO/QDs photoanode with ZnS and ZnSe passivation layers doped - Cu^{2+} in the range of 300–700 nm. Light is illuminated from the FTO substrate side, showing absorption dependence on the Cu^{2+} doping ratio. Below 550 nm, the absorption intensity slightly increases with Cu^{2+} content, possibly due to the formation of Cu^{2+} energy levels within the bandgap of ZnS and ZnSe. This result is consistent with the study on Sr doping in ZnSe for QDSSCs [14]. The FTO/ TiO_2 /QDs/ZnSe@ Cu^{2+} system exhibits enhanced absorption and a red shift in the 500–600 nm range. The FTO/ TiO_2 /QDs/ZnSe@ Cu^{2+} photoanode shows a higher absorption spectrum intensity than the FTO/ TiO_2 /QDs/ZnS@ Cu^{2+} photoanode. Overall, the doped anode films absorb longer wavelengths, extend into the visible light region, and result in a darker material.

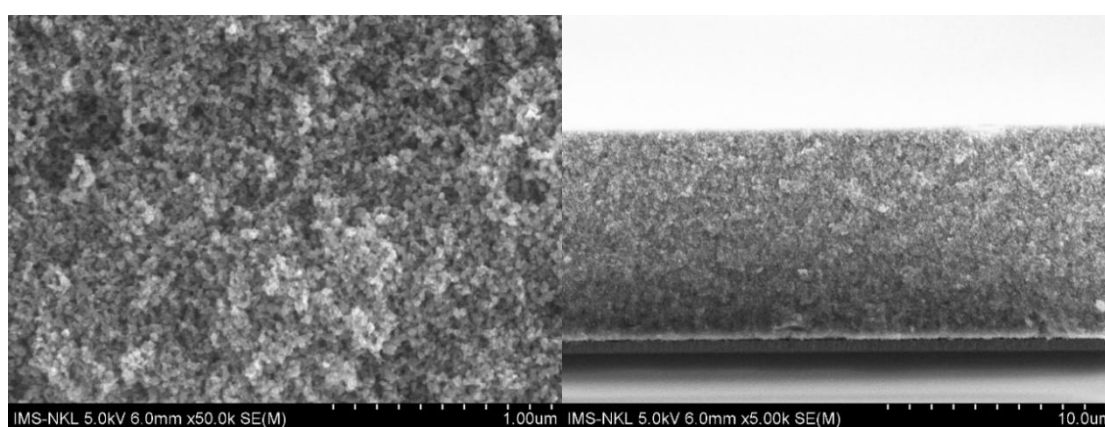


Figure 3. SEM images of the photoanode showing the surface and cross-section

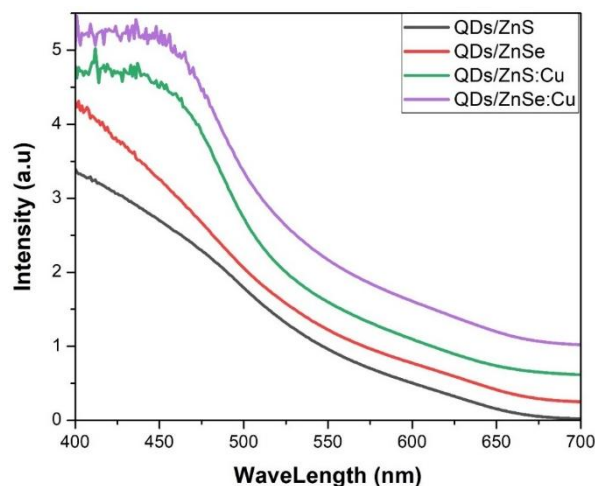


Figure 4. UV-Vis of X(S,Se) passivation layers doped - copper

X-ray diffraction (XRD) analysis was employed to investigate the structural characteristics of CdS, CdSe, $\text{ZnS}@ \text{Cu}^{2+}$, and $\text{ZnSe}@ \text{Cu}^{2+}$ quantum dots deposited on the TiO_2 surface. The diffraction patterns (Figure 5) confirm the crystalline nature of all samples. Specifically, five prominent diffraction peaks of TiO_2 observed at 25.354° , 37.785° , 48.077° , 53.922° , and 62.728° are indexed to the (101), (004), (200), (105), and (204) planes, respectively, corresponding to the anatase phase (JCPDS No. 00-004-0477) [15]. The cubic phase of CdS is identified by the characteristic (111) and (222) reflections at 26.5° and 54.5° , respectively.

(JCPDS No. 00-089-0440) [15], [16]. For CdSe, two peaks located at 27.2° and 42° are attributed to the (101) and (110) planes of the hexagonal structure (JCPDS No. 00-008-0459) [15]. Similarly, the hexagonal phases of ZnS and ZnSe are confirmed by peaks at 25.7° and 48.8° , which correspond to the (100) and (103) planes (JCPDS No. 00-089-2940) [14]. These results collectively demonstrate the successful deposition and crystallization of CdS, CdSe, ZnS@Cu²⁺, and ZnSe@Cu²⁺ quantum dots on the TiO₂ substrate.

The photovoltaic performance (J–V curves) of QDSSCs employing TiO₂/QDs/ZnS@Cu²⁺ and TiO₂/QDs/ZnSe@Cu²⁺ photoanodes was evaluated under standard solar illumination ($100 \text{ mW}\cdot\text{cm}^{-2}$), as summarized in Table 1 and Figure 6. The results indicate that the open-circuit voltage (V_{oc}) and fill factor (FF) exhibit minimal variation between the two systems; however, the conversion efficiency shows a marked dependence on the current density. Specifically, the TiO₂/QDs/ZnS@Cu²⁺ photoanode yields a current density of $22 \text{ mA}\cdot\text{cm}^{-2}$ and a corresponding efficiency of 4.5%, which is lower than that of the TiO₂/QDs/ZnSe@Cu²⁺ counterpart. Upon Cu²⁺ doping into the ZnSe passivation layer, both the current density and power conversion efficiency are significantly enhanced, achieving values of $23 \text{ mA}\cdot\text{cm}^{-2}$ and 5.3%, respectively. This improvement is attributed to the substitution of Zn²⁺ by Cu²⁺ in the crystal lattice, which reduces the film's internal resistance and introduces impurity energy levels within the bandgap of ZnS and ZnSe, thereby enhancing photon absorption. These findings are in good agreement with the study, which demonstrated that Cu²⁺ and Mn²⁺ doping in ZnS substantially increased the photocurrent density.

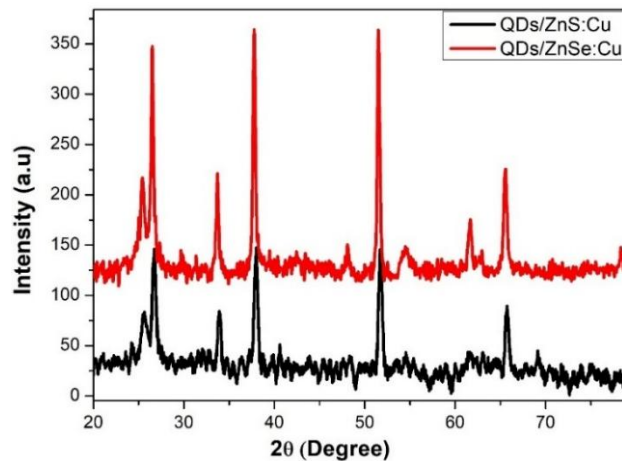


Figure 5. XRD spectra of X(S,Se):Cu passivation layers

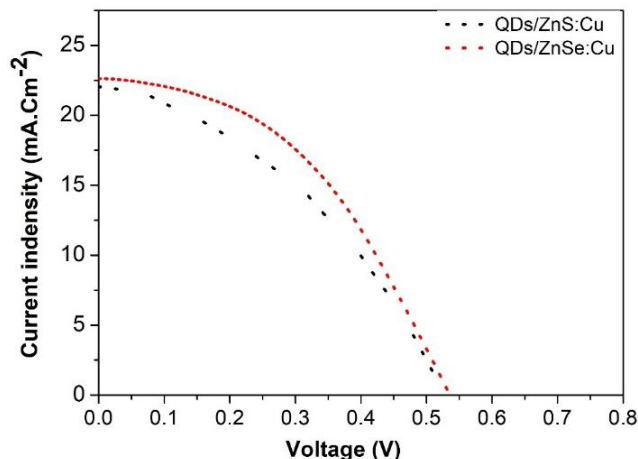


Figure 6. Photovoltaic performance of X(S,Se):Cu

Table 1. The characteristic parameters of devices

Sample	V _{oc} (V)	J _{sc} (mA·cm ⁻²)	FF	PCE (%)	R _{ct1} (Ω)	R _{ct2} (Ω)
Photoanode based ZnS:Cu	0.515	22	0.41	4.5	12	116
Photoanode based ZnSe:Cu	0.52	23.1	0.439	5.31	17	331

This study examines the electron transfer mechanisms within thin-film layers, including electron transport at the photoanode interface (R_{ct2}), electron diffusion in the electrolyte, and charge transfer at the cathode (R_{ct1}), through electrochemical impedance spectroscopy (EIS) under illumination at $100 \text{ mW} \cdot \text{cm}^{-2}$. The analysis (shown in Figure 7), conducted using EC-LAB software, reveals that electrodes coated with Cu^{2+} -doped ZnS exhibit lower charge transfer resistances (R_{ct1} and R_{ct2}) compared to those coated with Cu^{2+} -doped ZnSe, with minimum recorded values of $R_{ct1} = 17 \Omega$ and $R_{ct2} = 33 \Omega$ (Table 1). Concurrently, the current density and overall device efficiency improved notably, from $22 \text{ mA} \cdot \text{cm}^{-2}$ to $23 \text{ mA} \cdot \text{cm}^{-2}$. This enhancement is primarily attributed to the $\text{ZnS}@\text{Cu}^{2+}$ layers, which not only improve photon absorption but also contribute to light reflection, thereby increasing the effective light harvesting by the TiO_2/QDs photoanode [17]-[22].

Furthermore, the conduction band edge of $\text{ZnS}@\text{Cu}^{2+}$ is positioned higher than that of TiO_2/QDs , which helps suppress electron back diffusion and reduces recombination losses [13]. The incorporation of Cu^{2+} also induces a redshift in the absorption spectrum, extending into the visible light region, due to the formation of impurity levels within the bandgap of ZnS and ZnSe [23]. These results are consistent with the findings reported previously and demonstrate significantly improved efficiency compared to previous studies [24], [25].

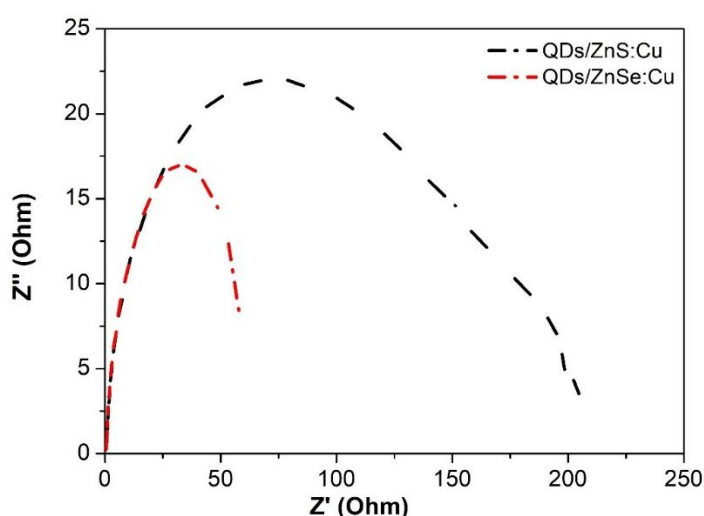


Figure 7. EIS of X(S,Se) passivation layers doped - copper

4. CONCLUSION

The Zinc(S,Se):Cu passivation layer was successfully fabricated using the SILAR method and applied to passivate the surface of CdS and CdSe quantum dots in the photoanode electrode. In addition to its protective role, the Zinc(S,Se):Cu layer also contributes to enhancing photon absorption in quantum dot solar cells. The absorption spectrum shows that the electrode with Zinc(S,Se):Cu exhibits a clear redshift of the absorption peak into the longer wavelength region of the visible spectrum compared to the undoped sample, which is consistent with the J-V results. Specifically, the current density increased to $23 \text{ mA}/\text{cm}^2$ and the efficiency rose to 5.3% with the application of Zinc(S,Se):Cu. These results highlight the role of the Zinc(S,Se):Cu layer in supporting light absorption. Furthermore, electrochemical impedance spectroscopy revealed the lowest dynamic resistance in the X(S,Se):Cu sample, indicating reduced recombination processes and more efficient electron transport. Finally, the structural properties, surface morphology, and film thickness were confirmed through XRD and FESEM analyses.

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AUTHOR CONTRIBUTIONS STATEMENT

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Name of Author	C	M	So	Va	Fo	I	R	D	O	E	Vi	Su	P	Fu
Ho Minh Trung	✓	✓	✓	✓	✓	✓		✓	✓	✓			✓	
Le Xuan Thuy			✓	✓	✓		✓	✓	✓	✓	✓	✓		✓

C : Conceptualization

M : Methodology

So : Software

Va : Validation

Fo : Formal analysis

I : Investigation

R : Resources

D : Data Curation

O : Writing - Original Draft

E : Writing - Review & Editing

Vi : Visualization

Su : Supervision

P : Project administration

Fu : Funding acquisition

CONFLICT OF INTEREST STATEMENT

Authors state no conflict of interest.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author, [LXT], upon reasonable request.

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BIOGRAPHIES OF AUTHORS



Ho Minh Trung    received the Ph.D. degree in physics from University of Science, Vietnam National University, Ho Chi Minh City, Vietnam. He is working as a lecturer at the Faculty of Basic Sciences, Vinh Long University of Technology Education, Vietnam. His research interests focus on developing the patterned substrate with micro- and nano-scale to apply for physical and chemical devices such as solar cells, OLED, photoanode. He can be contacted at email: trunghm@vlute.edu.vn.



Le Xuan Thuy    received the master degree in physics from Can Tho University, Vietnam. She received a Ph.D. from the Vietnam Academy of Science and Technology. She is working as a lecturer at the Faculty of Basic Sciences, Vinh Long University of Technology Education, Vietnam. Her research interests: solar cells, OLED, photoanode, and theory physics. She can be contacted at email: thuylx@vlute.edu.vn.